THE APPLICATION OF THE DIENYNE SYNTHESIS TO THE PRODUCTION OF PERHYDROPHENANTHRENE DERIVATIVES AND OTHER POLYNUCLEAR HYDROAROMATIC COMPOUNDS

BY

LAWRENCE ARTHUR PATTERSON

B.S., Montana State College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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INTRODUCTION

The treatment of substituted dienynes with acid hydrating agents has been found to give unsaturated cyclic ketones. The reaction has been used to prepare mononuclear and polynuclear hydroaromatic compounds. The possibility of preparing ring structures similar to those found in natural occurring compounds with physiological activity has been considered.

The structure of the unsaturated ketone obtained by the cyclization reaction has been the subject of controversy. The purpose of this investigation was to study this question of the structure of the cyclization products and to prepare additional polynuclear hydroaromatic compounds.

EXPERIMENTAL AND DISCUSSION

2-Naphthol was hydrogenated with Raney nickel to a mixture of the four geometric isomers of 2-decalol. Separation of this mixture into its isomeric forms was accomplished by the use of phthalic anhydride employing a modification of Hückel's method.[1] The two *trans* isomers were oxidized to *trans*-2-decalone and the two *cis* isomers to *cis*-2-decalone.

2-Ethynyl-*cis*-2-decalol and 2-ethynyl-*trans*-2-decalol were prepared by the method of Pearson[2] in which acetylene was added to the 2-decalone using potassium tertiary amylate as the catalyst. Three isomeric forms of the di-2-decalolacetylene were prepared by adding *cis*-2-decalone and *trans*-2-decalone to 2-ethynyl-*cis*-2-decalol. Dehydration of these three glycols with fused potassium acid sulfate gave three isomeric di-Δ^2-octalinylacetylenes ($C_{22}H_{30}$). Cyclization of these dienynes with sulfuric and acetic acids did not give the expected isomers of 2,3,6,7-dicyclohexan-$\Delta^{13,14}$-decahydro-9-phenanthrone ($C_{22}H_{32}O$). The products obtained gave no ketone derivatives and could not be identified. Dehydrogenation of the three cyclization products with palladized charcoal at 320° did not give the expected 2,3,6,7-dibenzophenanthrene ($C_{22}H_{14}$) which would result if the previously mentioned ketone had been

obtained. Instead, a crystalline partly dehydrogenated polynuclear hydroaromatic compound, analyzing for a spirane($C_{22}H_{18}$), was obtained.

Cyclization of di-Δ^1-1-cyclohexenylacetylene gave an α,β unsaturated ketone which was at first assigned a phenanthrene structure.[3] The work of Bogert [4,5] on the rearrangement of spirocyclohexane-1-1′-indane to phenanthrene during dehydrogenation has made the possibility of a cyclopentenone spirane structure quite likely. The synthesis of a perhydro-9-phenanthrone identical with the one obtained from the hydrogenation of the cyclization product was attempted in an effort to substantiate the phenanthrene structure of the cyclization product. The synthesis was carried out by converting diphenic acid anhydride to monomethyl diphenate which was then converted to the acid chloride. An Arndt-Eistert rearrangement of the acid chloride in the presence of methanol gave 2-carbomethoxymethyl-2′-carbomethoxybiphenyl. This ester was saponified and the sodium salt hydrogenated with Raney nickel to the perhydro acid. Heating the acid at 300-320° gave a perhydro-9-phenanthrone. This compound proved to be identical with the one obtained by White [6] when he also attempted a synthesis of the desired perhydro-9-phenanthrone.

SUMMARY

The cyclization of symmetrical dienynes containing the octalin ring proceeded in an anamolous manner giving products which could not be identified. The question of whether a phenanthrene or a cyclopentenone spirane structure exists for the cyclization product of di-Δ^1-1-cyclohexenylacetylene could not be definitely settled.

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VITA

The writer was born in Blaine County, Montana, June 30, 1915. He attended grammar school and high school at Chinook, Montana, and graduated in 1933. He attended Northern Montana College two years and then completed his work for a Bachelor of Science Degree at Montana State College in the year 1937. From 1937 to the present date he has been an assistant in inorganic chemistry at the University of Illinois while studying for the degree of Doctor of Philosophy.

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